DEVELOPMENT AND CHARACTERIZATION OF SULFONATED POLYETHERSULFONE MEMBRANE AS A POTENTIAL MATERIAL FOR DIRECT METHANOL FUEL CELL

ROSMAINIZA BINTI IBRAHIMI HUSAIMI

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Faculty of Chemical Engineering & Natural Resources

University Malaysia Pahang

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“I declare that this thesis entitled “*Development and Characterization of Sulfonated Polyethersulfone Membrane as a Potential Material for Direct Methanol Fuel Cell*” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature	:	……………………………………………
Name	:	ROSMAINIZA BT IBRAHIMI HUSAIMI
Date	:	16 MAY 2008

To my beloved mother and father

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ABSTRACT

Sulfonated polyethersulfone membrane is one of the potential candidates to be use as an electrolyte for fuel cell application due to its high thermal resistance. With a high heat deflection temperature of 400°F (204°C), it can withstand continuous exposure to heat and still absorb tremendous impact without cracking or breaking. Sulfonated polyethersulfone membrane has been prepared by conducting sulfonation process with sulfuric acid as a sulfonating agent and then the polymer precipitated had been dissolved in N-Methyl-2-pyrrolidone. The functional groups of sulfonic acids have been successfully incorporated in the PES backbone and detected using FTIR at 1033cm^{-1} wavelength. Membranes with 35.7% degree of sulfonation possess water uptake at the room temperature of 13.1 wt% and the value of IEC is about 11.43 mmol/g. The water uptake of the sulfonated polyethersulfone membrane increased with temperature from 13.1 wt% up to 46 wt%. Meanwhile, the methanol uptake was increased with an increased in concentration from 14.9 wt% to 26.2 wt%. Membranes prepared from SPES showed lower decomposition temperature and have good properties to be applied as a membrane for DMFC.

ABSTRAK

Polyethersulfone membran yang telah ditambah kumpulan asid sulfonic merupakan salah satu calon yang berpotensi untuk digunakan sebagai elektrolit untuk aplikasi bateri kerana mempunyai daya tahan yang tinggi terhadap haba. Dengan suhu pembiasan haba yang tinggi mencecah 400°F (204°C), ia dapat menahan pendedahan berterusan terhadap haba dan terus menyerap pelanggaran yang hebat tanpa retak atau pecah. Polyethersulfone membran disediakan dengan menjalankan proses penambahan kumpulan asid sulfonic dengan menggunakan asid sulfuric sebagai agen penambahan kumpulan asid sulfonic dan hasil turasan polimer dilarutkan menggunakan N-Methyl-2-pyrrolidone. Kumpulan fungsi untuk asid sulfonic yang telah disatukan ke dalam tunjang PES, di kesan menggunakan FTIR pada $1033cm^{-1}$. Membran dengan 35.7% kadar penambahan kumpulan asid sulfonic mempunyai kebolehan meyerap air sebanyak 13.1% pada suhu bilik dan nilai kadar perubahan ion adalah sebanyak 11.43mmol/g. Kebolehan polyethersulfone membran yang telah ditambah kumpulan asid sulfonic meyerap air meningkat apabila suhu bertambah dari 13.1% sehingga 46%. Pada masa yang sama, kebolehan polyethersulfone membran yang telah ditambah kumpulan asid sulfonic menyerap metanol meningkat apabila kepekatan methanol yang digunakan meningkat iaitu dari 14.9% sehingga 26.2%. Membran yang dihasilkan dari SPES mempunyai suhu pereputan yang rendah dan mempunyai ciri-ciri yang bagus untuk digunakan sebagai membrane untuk DMFC.

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W_{wet}	-	weight of the wet membranes
W_{dry}	-	weight of the dry membranes
str	-	strong
wk	-	weak
brd	-	broad
shp	-	sharp
M_{NaOH}	-	concentration of standard NaOH
W	-	mass of sample
V_{NaOH}	-	volume of NaOH solution used to neutralize

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Throughout the world, demand for power generation with environmental friendly is increased. This has encouraged research in various aspect of fuel cell. This is due to the reason that fuel cell is more clean compared to other power source. It can also helps reduce the usage of fossil fuel cell due to the high efficiency of energy conversion, low pollution level, low noise and low maintenance cost (Smitha *et al*., 2005).

Proton exchange membrane fuel cells (PEMFC) work with a polymer electrolyte membrane in the form of a thin, permeable sheet. This membrane is small and light, and it works at low temperatures (about 80°C, or about 175°F). Other types of fuel cells uses electrolytes which require temperatures as high as 1,000°C. The performance of PEM fuel cells which influenced by many parameters such as operating temperature, pressure and relative humidity of the gas stream.

Direct-methanol fuel cells or DMFCs are a subcategory of proton-exchange fuel cells where specially optimized PEFCs can be fed with methanol (or fuels with similar chemical structure), creating a so-called direct methanol fuel cell (DMFC). Conceptually, this could lead to a very simple system with a fuel that has a relatively high energy density and a liquid under ambient conditions (Appleby and Foulkes, 2004). However, the efficiency of direct-methanol fuel cells is low due to the high permeation of methanol through the membrane, which is known as methanol crossover.

At the current level of technology development, DMFCs are limited in the power that they can produce, but still can store much energy in a small space. This means DMFCs can produce a small amount of power over a long period of time. This makes them ill-suited for powering vehicles, but ideal for consumer goods such as mobile phones, digital cameras or laptops.

The recent categories of membrane that have been center of attention are perfluorinated ionomer (PFI) or perfluorosulfonated compounds (PFSA), non-fluorinated hydrocarbons, sulfonated poly(arylenes) and acid based complexes. Right now, the best choice polymer to be used as fuel cell membrane is Nafion which is perfluorinated membranes. Nafion is a strong, stable in oxidation and reduction and also good in proton conductivities. The problem is, Nafion has a temperature limitation. The crossover problem and loss of hydration occur at 100 °C (Sakari *et al*., 1985). It also expensive due to the operation catalys is noble-metal catalyst (typically platinum) to separate the hydrogen's electrons and protons (Smitha *et al*., 2005).

Therefore, a low cost polymer membrane that can outlast at high temperature is sought off. Among the alternatives candidates are polysulfone, polyphenylsulfone, polyethersulfone, polyether and polyetheryetherketone.

1.2 Problem statement

Demand for power generation with environmental friendly is increased which leading to the growing in research and using of fuel cell as a one of clean source of power generation. Currently, Nafion was the state of the art membrane for fuel cell. However, Nafion have a temperature limitation and high cost in production. Therefore, low cost polymer membrane that can outlast at high temperature is needed in order to overcome this problem.

1.3 Objective of Study

The objective of this study is to develop and characterize the sulfonated polyethersulfone membrane as a potential ion exchange membrane for DMFC fuel cell application.

1.4 Scopes of Study

There are some scopes which need to be a focused in order to meet the objective:

(a) Develop and characterize sulfonated polyethersulfone polymer as a membrane for direct methanol fuel cell (DMFC)
(b) Study the physicochemical of sulfonated polyethersulfone membrane for fuel cell application

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Types and Application

In medicine, microbiology, cellular physiology and biochemistry a membrane is a thin layer that separates various cellular structures or organs. It usually includes lipid bilayer reinforced by proteins and other macromolecules, and can refer to:

a) Basement membrane, the combination of the basal lamina and lamina reticularis or of two basal laminae
b) Biological membrane
c) Mucous membrane
d) Skin, part of the integumentary system

Membrane may also refer to artificial, semipermeable membranes which are used to separate species in a fluid on the basis of size, charge or other characteristics. Membrane have a multipurpose usage such as membrane for separation, filtration and also for fuel cell electrolyte. In separation, membrane acts as a barrier for two certain particles. The bigger particle will be block and the small particle will pass through the membrane. Figure 2.1 show the separation using membrane.

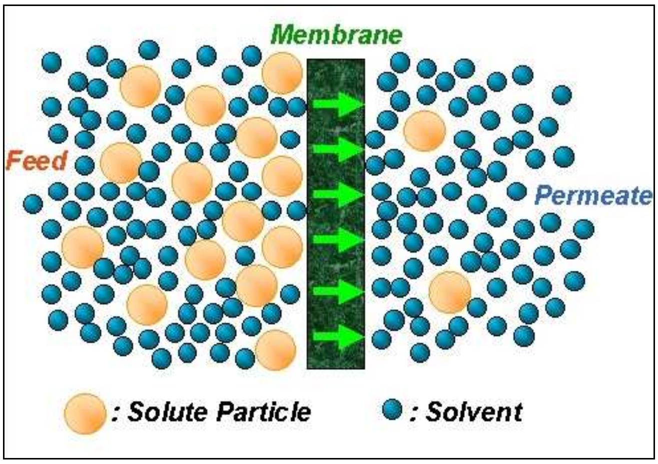

Figure 2.1 : Separation process using membrane

In separation, the membrane acts as a semipermeable barrier and separation occurs by membranes controlling the movements of various two molecules between two liquid phase, gases phase or liquid and gases phase (Geankoplis, 2003). Most separation processes are aiming at one of two results which are to collect the liquid (the filtrate) or to collect the retained sludge (the retentate).

Such membranes are employed in a range of applications from water and wastewater treatment like reverse osmosis, diffuser (sewage), landfill liners, nanofiltration, ultrafiltration and microfiltration to hydrogen fuel cells (proton exchange membrane).

2.2 Background of Fuel Cell

The fuel cell can trace its roots back to the 1800's. A Welsh born, Oxford educated barrister, who practiced patent law and also studied chemistry named Sir William Robert Grove realized that if electrolysis, using electricity, could split water into hydrogen and oxygen then the opposite would also be true. Combining hydrogen and oxygen, with the correct method, would produce electricity. To test his theory Sir William Robert Grove built a device that would combine hydrogen and oxygen to produce electricity, the world's first gas battery as shown in Figure 2.2, and then later renamed as fuel cell.

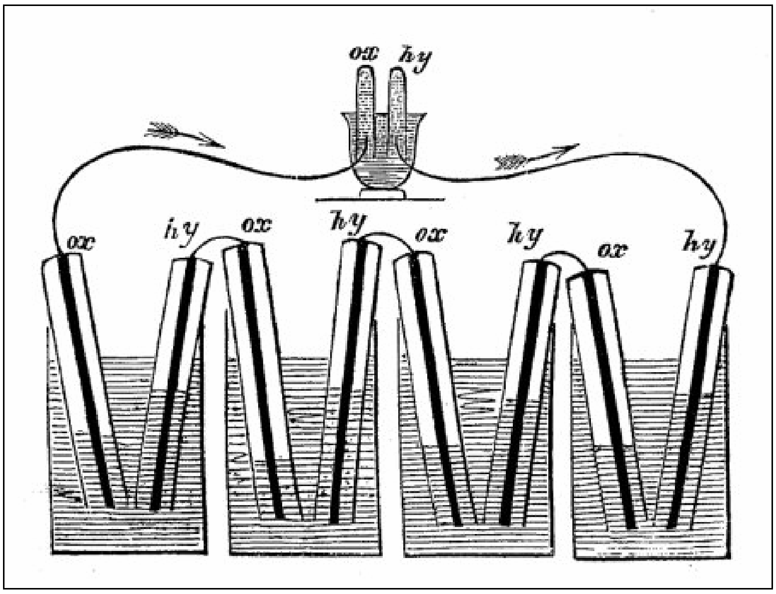

Figure 2.2 : William Grove's 'gas battery', the first fuel cell

Fast-forwarding to the 1960's, a new government agency was about to undertake the first step in maturing fuel cell technology. The National Aeronautics and Space Administration (NASA) were developing the mission critical systems for the first prolonged manned flight into space. Once in space, the orbiter needed a source of electricity. Batteries were ruled out due to the size, weight and toxicity necessary to support a mission of eight days in space. Photovoltaic were not practical, at the time, due to the size and weight of the solar panels necessary. Then fuel cell became the technological solution to NASA's dilemma of how to provide power for extended missions to space.

The earlier problems of cost and fuel supplies that plagued fuel cells became irrelevant as the spacecraft was already carrying liquid hydrogen and oxygen. An additional benefit of fuel cells over other technology was that the astronauts could consume the fuel cell's water by-product. Since their adoption by the space program, fuel cell technology has achieved widespread recognition by industry and government.

Though fuel cells in principle, could process a wide variety of fuels and oxidants, but the most interest today are those fuel cells that use common fuels or hydrogen as a reductant, and ambient air as the oxidant. Most fuel cell power systems comprise a number of components:

a) Unit cells, in which the electrochemical reactions take place
b) Stacks, in which individual cells are modularly combined by electrically connecting the cells to form units with the desired output capacity
c) Balance of plant which comprises components that provides feed stream conditioning (including a fuel processor if needed), thermal management, and electric power conditioning among other ancillary and interface functions

Operating principle of the fuel cell is the fuel electrode (anode) and the oxygen electrode (cathode) which is interconnected by an ion-conducting electrolyte. The electrodes are electrically coupled to an electricity consumer by external metallic lines outside the cell. In this section of the electric circuit, the electric current is transmitted by the electrons whereas in the electrolyte the current transfer is affected by means of ions. Figure 2.3 shows the principle of a fuel cell. The anode is supplied with hydrogen as the fuel gas which is electrochemically split into protons and electrons at the electrode/electrolyte interface. The electrons which perform electrical work in the outer electric circuit are passed into the cathode where they reduce the oxygen into water at the electrode/electrolyte interface.

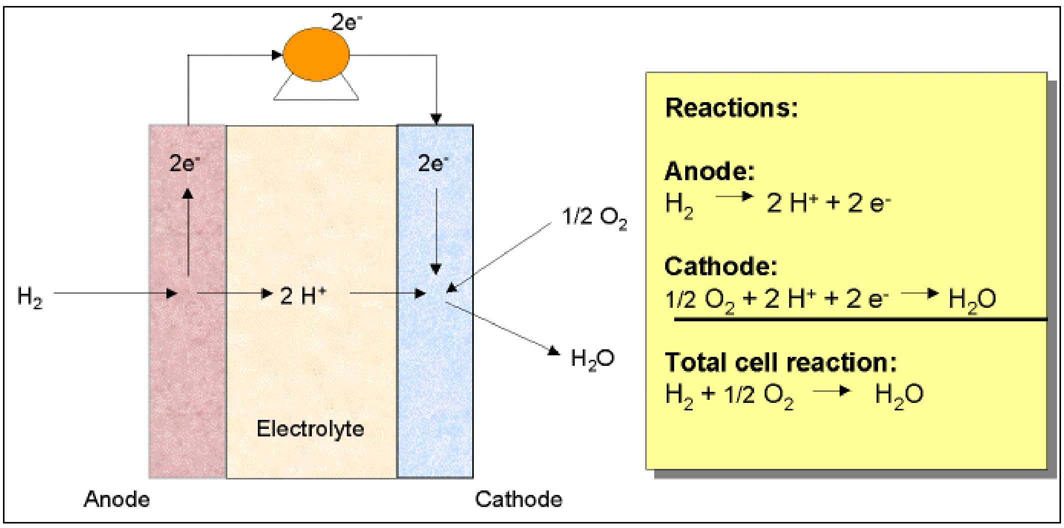

Figure 2.3 : Operating principles of fuel cell

The required protons come from the anode through the electrolyte. As can be seen from the schematic, the electrodes must also be permeable to gas, i.e. porous. A fuel cell reaction normally requires all three phases to be present which is the solid phase (electron conductor), the liquid phase (ion conductor) and the gas phase (electrode pores).

2.3 Types of Fuel Cell

A variety of fuel cells are in different stages of development. The most common classification of fuel cells is by the type of electrolyte used in the cells such as polymer electrolyte fuel cell (PEFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC). Broadly, the choice of electrolyte dictates the operating temperature range of the fuel cell. The operating temperature and useful life of a fuel cell dictates the physicochemical and thermo mechanical properties of materials used in the cell components (i.e., electrodes, electrolyte, interconnect, current collector, etc.). Aqueous electrolytes are limited to temperatures of about 200 °C or lower because of their high vapor pressure and rapid degradation at higher temperatures. The operating temperature also plays an important role in dictating the degree of fuel processing required. In low-temperature fuel cells, all the fuel must be converted to hydrogen prior to entering the fuel cell. In addition, the anode catalyst in low temperature fuel cells (mainly platinum) is strongly poisoned by CO. In high-temperature fuel cells, CO and even CH_4 can be internally converted to hydrogen or even directly oxidized electrochemically. Table 2.1 provides an overview of the key characteristics of the main fuel cell types (Appleby and Foulkes, 2004).

Table 2.1 : Summary for different type of fuel cell (Appleby and Foulkes, 2004)

	PEFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Hydrated Polymeric Ion Exchange Membranes	Immobilized Potassium Hydroxide in asbestos matrix	Immobilized Liquid Phosphoric Acid in SiC	Immobilized Liquid Molten Carbonate in $LiAlO_2$	Perovskites (Ceramics)
Electrodes	Carbon	Transition metals	Carbon	Nickel and Nickel Oxide	Perovskite and perovskite /metal cermet
Catalyst	Platinum	Platinum	Platinum	Electrode material	Electrode material
Interconnect	Carbon or metal	Metal	Graphite	Stainless steel or Nickel	Nickel, ceramic, or steel
Operating Temperature	40 – 80 °C	65°C – 220°C	205 °C	650 °C	600-1000 °C
Charge Carrier	H+	OH-	H+	CO_3=	O=
External Reformer for Hydrocarbon fuels	Yes	Yes	Yes	No, for some fuels	No, for some fuels
External Shift conversion of CO to hydrogen	Yes, plus purification to remove trace CO	Yes, plus purification to remove CO and CO2	No	Yes	Yes
Prime Cell Components	Carbon-based	Carbon-based	Graphite-based	Stainless based	Ceramic
Product Water Management	Evaporative	Evaporative	Evaporative	Gaseous Product	Gaseous Product
Product Heat Management	Process Gas + Liquid Cooling Medium	Process Gas + Electrolyte Circulation	Process Gas + Liquid cooling medium or steam generation	Internal Reforming + Process Gas	Internal Reforming + Process Gas

2.3.1 Proton Exchange Membrane Fuel Cell

The PEM fuel cell gained prominence after General Electric (GE) invented a small fuel cell for a program with the U.S. Navy's Bureau of Ships (Electronics Division) and the U.S. Army Signal Corps in 1960s. Based on its simplicity design, weight advantages and combined with optimum compability, PEM fuel cell can be use in many applications. Figure 2.4 shows the schematic overview of PEM fuel cell.

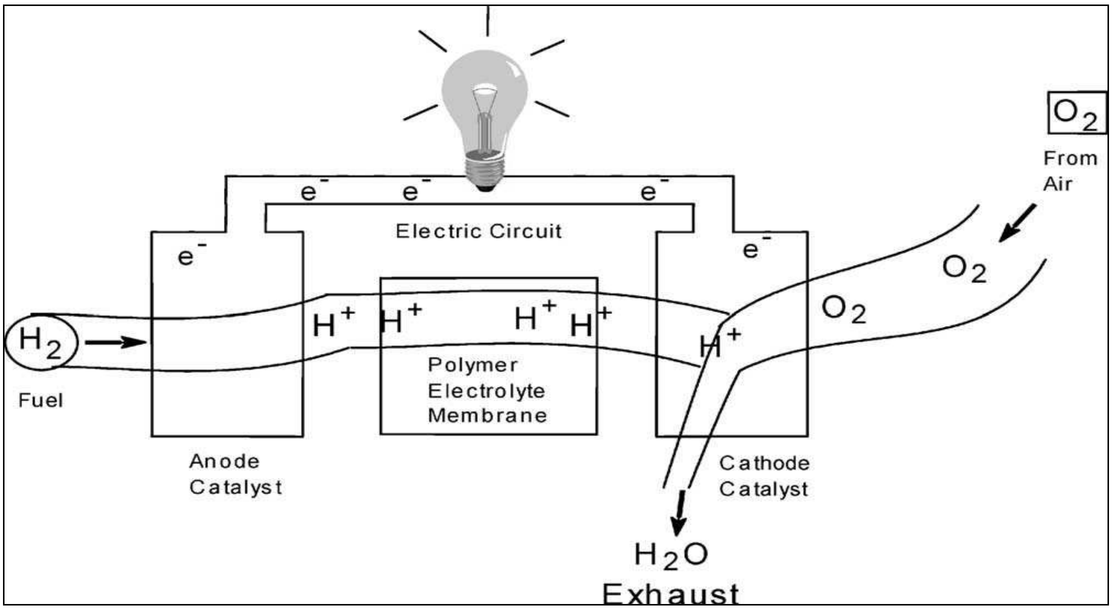

Figure 2.4 : Schematic view of proton exchange membrane fuel cell

PEM fuel cell technology differentiates itself from other fuel cell technologies in that a solid phase polymer membrane is used as the cell separator/electrolyte. Because the cell separator is a polymer film and the cell operates at relatively low temperatures, issues such as sealing, assembly, and handling are less complex than most other fuel cells. The need to handle corrosive acids or bases is eliminated in this system. PEFCs typically operate at low temperatures (60°C to 80°C), allowing for potentially faster startup than higher temperature fuel cells. The PEM fuel cell is seen as the main fuel cell candidate technology for light-duty transportation applications. While PEM fuel cell are particularly suitable for operation on pure hydrogen, fuel processors have been developed that will allow the use of conventional fuels such as natural gas or gasoline.